

THE NATURE OF RESINS AND ASPHALTENES

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In 1944, Zavoisky [1] discovered electronic paramagnetic resonance (EPR), a tool for direct detection of unpaired electrons in molecular systems, which gave rise to a new avalanche of studies on radical reactions and paramagnetic phenomena, and in 1957 Garif'yanov and Kozyrev [2] found unpaired electrons in petroleum-like systems and thus proved the presence of free radicals in these systems. Thereafter, the role of radicals in petroleum-like systems was discussed rather [for example 3, 4]. However, it could not be evaluated adequately because of the absence of any methodical basis for correct determination of the number of unpaired electrons in the petroleum-like system under investigation. Thus, Flinn et al. [5], based on the published estimate for the paramagnetism of asphaltenes 10^{18} spins/g, arrived at the conclusion that for every 100 molecules there is one free radical. This estimate gave rise to the wide-spread opinion that the role of paramagnetics in asphaltene structures is insignificant. However, once a method for rigorous quantitative estimation of the fraction of paramagnetic molecules has been developed [6], the paramagnetism of petroleum-like systems is estimated as 10^{15} (for gasolines), 10^{17} - 10^{18} (for oils), 10^{19} - 10^{21} (for asphaltenes), and 10^{20} - 10^{22} spins/g (for carbenes-carboids, some cokes, and insoluble carbonic materials). Even for some petroleum (e.g., Archinskoe petroleum of Tomsk region), the paramagnetism is abnormally high 10^{21} spins/g, which is a direct indication of the specific role played by paramagnetic molecules in petroleum-like systems.

Other evaluations of asphaltene-resin systems are the following.

- a. Those systems have no FREE IONS, namely the dissociation of molecules by action of the kinetic energy movement does not go through the heterolytic mechanism, but through the homolytic mechanism.
- b. The experiments show that organic acids and bases concentrate not in asphaltenes, but into maltenes with minimum of their contents into the resins (carbon radioactive label), namely the oil systems (with the asphaltenes and resins) contain minimum (or zero) amount of polar molecules. This is confirmed by the value of dielectric constant of oil systems, which is close to benzene.
- c. The quantummechanic calculations show, that the potential energy of attraction between the molecules of compounds in oil systems maybe the following:
 1. Ion-ion. ATTRACTION. However, the ions are absent.
 2. Radical+radical. ATTRACTION. Radical existing in the system and those formed as a result of homolytic reactions, recombine or transition into the singlet state or associate depending on volume restrictions.
 3. Radical+charge-polarised molecules. ACIDATION. Therefore organic acids and bases concentrate into the maltene parts, but only minimum of their amount is found in resins.
 4. Radical+charge and spin-neutral molecules. ACIDATION. Therefore, the radicals are rejected from the saturated carbon hydrogenates and other compounds with large dielectric constants. Under industrial conditions this process is entitled "DEASPHALTISATION".
 5. Radicals+spin-polarised molecules. ATTRACTION. On this basis colloid particles of oil systems are built with radicals in the centre of a particle, surrounded with aromatic and heteroorganic molecules.
 6. Spin-polarised+spin-polarised molecules. The DIFFERENT DEGREE OF THE ENERGIES of ATTRACTION. On this basis circumference stratum of colloid particles are built.
 7. Spin-polarised+spin-neutral molecules. LITTLE, TILL TO ZERO ENERGIES OF ATTRACTION. On this basis the combination of the circumference stratum of colloid particles with encircling medium is built (with the paraffin-naphthene saturate hydrocarbons, in particular with maltenes in oil systems). A universal theoretical picture the common equation of potential energies maybe given for interaction between molecules:

$$V = K_0 e^{-kr} + K_1 r^{-1} + K_2 r^{-2} + K_3 r^{-3} + K_4 r^{-4} + K_5 r^{-5} + K_6 r^{-6} \quad (1)$$

where: k, K - coefficients, e - natural logarithm, r - distance between the interaction centres. The coefficient "K" may be either "+" or "-". The latter denotes attraction.

The Zero member beats reflects exchangeable interactions between radicals, the first - charge between ions, the second - between ions and charge-polarised molecules, the third - between radicals and spin-polarised molecules, the fourth and fifth - between breakwater molecules with different degree of spin and charge polarization (multipole members), and the sixth - between neutral molecules (Van-der-Vaals member).

d. From quantum mechanics considerations the virial-theorem for compound-mixtures must be followed:

$$\langle T \rangle = 1/2 n \langle V \rangle \quad (2),$$

where "n" is the number of grade on the variable "r" in formula (1) with allowance for the sign of grade, and "T" - kinetic energy. The brackets $\langle \rangle$ denote the middle meanings of energies.

Out of formula follows the strict necessity of coordination of acts for the alteration of potential energies of attraction-acidation between molecules and of the kinetic energies of their movement with distance between interacting molecules in physical-chemical processes, into this numerals homolytise, heating, cooling, in chemical reactions and etc.

e. Molecules with unpaired spin will not give NMR-spectra (coordinately with quantum mechanics considerations). The oil samples with high number of spins give weak (low intensity) NMR-spectra, what is attributed from the few contribution of diamagnetic molecules (some of asphaltenes will not give NMR-spectra at all), that is well coordinated with theory. The theoretical and experimental results allow estimation and understanding of the nature of resins and asphaltenes in oil dispersed systems.

The contradictory explanation of the colloidal structures of petroleum systems in terms of charge phenomena (electrolytic dissociation, donor-acceptor interactions, hydrogen charge-dipole interactions, etc.) called for both a new theoretical base and a complex comprehensive interpretation of the information obtained by chemical and instrumental methods for analyzing petroleum, petroleum products, resins, asphaltenes, and other petroleum-like materials, which has been reduced to several basic principles that are in excellent agreement with all available experimental data. These principles are discussed here.

There is no doubt that, the process of excitation and/or homolytic dissociation is a process actually identifiable with the use of instruments intended for physical investigations; second, from theoretical (quantum mechanical) reasonings it should be stated that this process fails not to occur, and, third, this process does occur on introduction of a solvent into a disperse petroleum system and/or its heating. Therefore, the statement is valid that the study of the interaction of the molecules of the solvent introduced with the molecules of associative combinations under varied conditions may be of primary importance for the technology of raw petroleum transformation in the near future.

In view of the importance of these results for the chemistry of solvents, in particular, petroleum, we present below the fundamental aspects of the chemistry of petroleum-like systems inherent in any non-water solutions and in some low-polarity water solutions.

1. Asphaltenes (being a type of powder) are not involved as components in petroleum (petroleum-like) systems, but they are formed in the process of action of a solvent on the system as associative combination of molecules having a higher density than the solution and separated from the system to form a precipitate.

2. The reason for the appearance and existence of asphaltenes is the presence of paramagnetic molecules that have positive potential energies of interaction with respect to saturated hydrocarbon molecules (repulsion) or other type molecules with sigma-bound atoms.

3. The possibility for the prolonged existence of paramagnetic molecules in the medium of diamagnetic molecules is provided by a shell preventing radicals from recombination. The shell is formed by the same principles as the solvate shells in electrolytic solutions, but the forces therewith are quantum (exchange) rather than charge in nature. Low-activity radicals may have thin shells or none at all. Active radicals will have heavy shells; in their nearest vicinity there will be accumulated molecules with a high energy of interaction with paramagnetic molecules, and the interaction energy will decrease in going to the periphery of the associative combination of molecules. If the associate density is comparable with the medium density, no separation will

occur, and the paramagnetic molecule will be able to exist for an infinitely long time in the center of the associate and will not recombine notwithstanding its high activity.

4. Diamagnetic molecules which go into the triplet state or dissociate into radicals under minor energy actions (e.g., on the order of a dozen of kilojoules per mole) are the basic molecules consisting resins. Owing to the kinetic energy of molecules, paramagnetic molecules are always present in small amounts in resins, that appear and due in equilibrium homolysis-recombination reactions. The range of energies required for a molecule to go into the triplet state or to dissociate into radicals may be rather large in view of the variety of molecules; so asphaltenes (precipitates) may occur from resins under the action of saturated solvents at elevated temperatures in substantial amounts. However, the molecules of such precipitates, when the original low-temperature conditions are reverted, recombine to transform again into the resin diamagnetic molecules.

5. Resins are a potential source for asphaltenes owing to the high probability of homolytic processes; asphaltenes are a potential source for resins owing to the molecules present in the nearest surrounding of radicals in associative combinations.

6. The properties of resins and asphaltenes are fundamentally independent of the atomic composition but depends on the energy of the interaction of atoms in molecules and molecules with one another. The varied element composition of resins and asphaltenes from various raw materials imparts them some specific properties, but the principles of appearance and existence of these associative combinations are almost independent of the composition.

7. All properties of resins and asphaltenes are well explained by the quantum mechanical principles of the formation of homopolar interactions and fail to be explained in terms of heteropolar interactions.

8. The properties of asphaltenes and resins are inherent in all types of viscous and liquid homopolar systems (petroleums, tars, homopolar schistose resins, homopolar carbonic hydrogenation products, etc.) and have an universal nature.

9. The properties of homolytes and the regularities of the formation of associative combination in them dictate some rules for the application of instrumental techniques whose violation may result in artifacts.

- Spectral characteristics (intensities of peaks and their positions on the frequency or angle axis) should be calculated (measured) with respect to quantitative references.

- The references should not be introduced they may change (sometimes substantially) the system properties. For solid systems no changes of this type were noticed, with the exception of asphaltenes being concentrates of paramagnetic molecules with variable paramagnetism.

- To obtain the spectral characteristic of a material, it is necessary to use a complete referenced spectrum. If a partial spectrum is used, even with referencing it is impossible to estimate the contribution of a given parameter into the properties in total. If this contribution is small and this has been overlooked, an artifact is unavoidable.

10. The paramagnetic nature of disperse homolytes, the peculiarities of the physical chemistry of the prohibited singlet-triplet and triplet-singlet transitions (diamagnetic-to-paramagnetic and reverse transitions of molecules) in petroleum-like systems, as well as, the quantum mechanical prohibitions for the filling of phase spaces by bosons, fermions, and paulions offer the possibility to predict certain types of chemical interactions in such systems.

- The presence of molecules with a high degree of spin polarization and with unpaired electrons is responsible for the amphoteric nature of the properties of petroleum-like systems. Thus, the compounds precipitated on acid impregnates behave like the compounds precipitated on base impregnates. In a detailed analysis it is generally revealed that these are the same compounds which are precipitated in a way inherent in the precipitation of the high-polarity molecules whose high polarity is due to the readiness of forced charge polarization. Note that for this type of compounds both the ionization potential and the electron affinity are low.

- In petroleum-like liquid mixtures, molecules with pronounced charge polarization or electrolytic dissociative ions are practically absent. All electrophoretic and electrical conductance phenomena in these systems are the consequence of the field-assisted charge polarization of various spin-polarized molecules and radicals. Therefore, both the cathode and the anode masses strongly vary qualitatively and quantitatively with electric field to the extent that the direction of

precipitation is changed which requires significant potentials, some orders of magnitude higher than those required for electrolytic dissociation.

-All reactions with petroleum-like media are homolytic in nature, and the touch of heterogeneity in them is conditioned by the pronounced charge properties of specially used electrolytic reagents. However, the propositions of the ionic mechanism are often not justified even for ferric chloride, sulfuric acid, and the like. A study of catalytic reactions should also be performed with due account of the regularities revealed.

11. As leads for further research, besides pending studies of already raised problems, it is noteworthy to develop adequate quantum mechanical and physicochemical models to describe:

- the DPS states;
- homolytic processes and the possibility of affecting their passage by fields;
- the thermolytic reactions in the existing chemical works;
- the catalytic reactions in the existing and predicted chemical works;
- the mechanism of action of additives for stabilization, inhibition, inflammation, quenching, ignition, etc;
- the DPS compounds showing the properties of radicals, biradicals, and spin-polarized particles with high and low degrees of spin polarization and the places of these compounds in the DPS.

12. The most important line of studies, going far beyond petroleum chemistry, is research in the field of theory of liquids. It is for the first time since the impressive studies on electrolytic dissociation performed by Arrhenius that we may say that homolytic dissociation has equally attracted the attention of researchers and the possibility has appeared to develop a unified theory of dissociation based on the available and future achievements in quantum mechanics with the goal to gain an understanding of the structure of liquid systems of any origin.

In conclusion, we present several figures illustrating some experimental results to confirm the above fundamental inferences on the paramagnetic nature of the dispersions in petroleum-like systems.

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